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(54) Addition polymerization catalyst with oxidative activation.

(57) Addition polymerization catalysts of the formula $L_n MX^+ A^-$ prepared by oxidation of a Group 4 or Lanthanide metal derivative of the formula $L_n MX_2$ with an oxidizing agent of the formula $(Ox^+)_b(A^-)_d$ are free of interfering amine byproducts. In these formulae:-
 L independently each occurrence is a ligand or ligand system, especially a η^5 -cyclopentadienyl group optionally covalently bonded to M through a substituent;
 n is an integer, especially 1;
 M is a Group 4 or Lanthanide metal, especially titanium or zirconium;
 X is a hydride or a hydrocarbyl, silyl or germyl group having up to 20 carbon, silicon or germanium atoms, especially benzyl;
 A⁻ is a monovalent compatible noncoordinating anion, especially perfluorotetraphenyl borate;
 Ox⁺ is a cationic oxidizer having a charge (+8), especially Ag⁺ or ferrocenium;
 A⁺ is a compatible noncoordinating anion; and
 b and d are integers selected to provide charge balance.

EP 0 468 651 A1

This invention relates to compositions of matter that are useful as catalysts, to a method for preparing the compositions of these catalysts, and to a method of using the compositions as addition polymerization catalysts. More particularly, this invention relates to catalyst compositions, to a method of preparing these catalyst compositions and to a method for polymerizing olefins, diolefins and/or acetylenically unsaturated monomers wherein these catalysts are used.

The use of Ziegler-Natta type catalysts in the polymerization of addition polymerizable monomers is, of course, well known in the prior art. In general, these soluble systems comprise a Group 4 or Lanthanide metal compound and a metal alkyl cocatalyst, particularly an aluminum alkyl cocatalyst.

In EP-A-0277,004 there are disclosed certain bis(cyclopentadienyl) metal compounds formed by reacting a bis(cyclopentadienyl) metal complex with salts of Bronsted acids containing a non-coordinating compatible anion. The reference discloses the fact that such complexes are usefully employed as catalysts in the polymerization of olefins. For the teachings contained therein the aforementioned EP-A-0277,004 is herein incorporated in its entirety by reference thereto.

Disadvantageously it has now been found that catalysts prepared according to the foregoing technique are detrimentally affected by the presence of by-product amine or phosphine compounds resulting from the catalyst formation. That is, the procedure of EP-A-0277,004 involves an irreversible reaction between a ligand of the metal compound and a cation of the Bronsted acid salt. In practice such cations are generally trialkyl ammonium or phosphonium ions that result in the formation of a tertiary amine or phosphine by proton transfer to the ligand during catalyst formation. Such amine or phosphine compounds are undesirable components of the resulting catalyst due to their inhibiting effect on addition polymerizations.

It would be desirable if there were provided a addition polymerization catalyst that is activated in a manner that forms only noninterfering and inert by-products.

In *J. Am. Ch. Soc.* 109, 4111-4113 (1987) there is disclosed a process for preparation of cationic zirconium (IV) benzyl complexes by one electron oxidation of d^0 organometallic compounds. The solvents employed in the preparation of the zirconium metallocenes were tetrahydrofuran or methylene chloride both of which interfere with the desired catalyst formation and/or detrimentally affect subsequent olefin polymerizations. In addition the reference employed an oxidizing agent containing tetraphenylborate. Such anions, it has now been discovered, are unacceptable for use in an oxidation activation process for preparing addition polymerization catalysts.

It has now been discovered that the foregoing and other disadvantages of the prior art ionic olefin polymerization catalysts can be avoided or at least reduced with the catalysts of the present invention. In addition an improved catalyst activation procedure and improved addition polymerization processes are provided according to the present invention. It is, therefore, an object of this invention to provide improved ionic catalyst systems which are useful in the polymerization of addition polymerizable monomers including olefins, diolefins and/or acetylenically unsaturated monomers. It is another object of this invention to provide a method for preparing such improved catalysts. It is a further object of this invention to provide an improved polymerization process using such improved catalysts. It is still another object of this invention to provide such an improved catalyst which is not subject to formation of interfering compounds. Finally it is an object of this invention to provide such an improved catalyst which may permit better control of the product polymer molecular weight and molecular weight distribution.

In accordance with the present invention there is provided a catalyst useful for addition polymerizations, which catalyst is substantially lacking in amine byproducts, said catalyst corresponding to the formula:

$L_f MX^+ A^-$, wherein:

L independently each occurrence is a ligand or ligand system;

M is a metal of group 4 or Lanthanide series of the Periodic Table of the Elements;

X is hydride or a hydrocarbyl, silyl or germyl group having up to 20 carbon, silicon or germanium atoms;

f is an integer greater than or equal to 1; and

A^- is a monovalent compatible noncoordinating anion.

Preferably M is a metal of group 4 of the Periodic table of the Elements, most preferably titanium or zirconium. Also, preferably X is hydride or C_1-C_{10} hydrocarbyl.

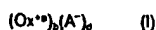
Further in accordance with the present invention there is provided a process for preparing the above addition polymerization catalyst comprising contacting a derivative of a group 4 or Lanthanide metal corresponding to the formula:

$L_f MX_2$, wherein

L, f, M, and X are as previously defined,

with an oxidizing agent which in reduced form is noninterfering with the resulting catalyst, said oxidizing agent comprising a cationic oxidizer and a compatible noncoordinating anion.

The oxidizing agent corresponds to the formula:



wherein:

Ox^{+a} is a non-Bronsted acid, cationic oxidizer having a charge of (+a) capable of oxidising the derivative of a Group 4 or Lanthanide metal;

5 A^- is as previously defined; and

b and d are integers selected to provide charge balance.

The catalysts may be prepared by contacting the derivative of a Group 4 or Lanthanide metal with the oxidizing agent optionally in an inert diluent such as an organic liquid.

10 All reference to the Periodic Table of the Elements herein shall refer to the Periodic Table of the Elements, published and copyrighted by CRC Press, Inc., 1989. Also, any reference to a Group or Groups shall be to the Group or Groups as reflected in this Periodic Table of the Elements using the IUPAC system for numbering groups.

The term "ligand or ligand system" refers to any ancillary, electron donating or electron sharing moiety. Such ligands include anionic ligands and neutral donor ligands.

15 Illustrative but non-limiting examples of suitable anionic ligands include: R , $-R'(OR')_mOR$, $(OR')_nOR$, $-PR_2$, $-SR$, $-OR$, $-NR_2$, hydride, and organometalloid radicals comprising a Group 14 element wherein each of the hydrocarbyl substituents contained in the organic portion of said organometalloid, independently, contains from 1 to 20 carbon atoms. In these ligands:

20 R is a hydrocarbyl, silyl, germyl or a substituted hydrocarbyl, silyl, or germyl group of from 1 to 24 carbon, silicon, or germanium atoms;

R' is C_{2-10} alkylene, and

m is an integer from zero to ten.

Illustrative but non-limiting examples of suitable neutral donor ligands (L') include: ROR , NR_2 , PR_3 , and SR_2 wherein R is as above defined.

25 The term "cationic oxidizer" as used herein refers to an organic or inorganic ion having an oxidation potential sufficient to cause a molecular oxidation of the derivative of a Group 4 or Lanthanide metal so as to form a catalytic species. Generally and preferably the Group 4 or Lanthanide metal of the derivative compound is already in the highest atomic oxidation state. The process of the invention involves a molecular oxidation. Most preferred cationic oxidizers have an oxidation potential of at least +0.20 volt and preferably at least +0.25 volt. Cationic oxidizers are not Bronsted acids.

As used herein, the recitation "compatible noncoordinating anion" means an anion which when functioning as a charge balancing anion in the catalyst system of this invention does not transfer an anionic substituent or fragment thereof to any cationic species thereby forming a neutral Group 4 or Lanthanide metal product. "Compatible anions" are anions which are not degraded to neutrality during catalyst preparation or use.

35 The recitation "metalloid", as used herein, includes nonmetals such as boron, phosphorus and the like which exhibit semi-metallic characteristics.

Further preferred derivatives correspond to the formula: L^*MX_2 , wherein:

L^* is a derivative of a substituted cyclopentadienyl or similar delocalized π -bonding group imparting a constrained geometry to the metal active site and containing up to 20 nonhydrogen atoms; and

40 M and X are as defined above.

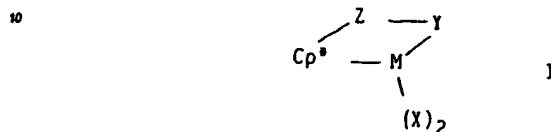
By use of the term "constrained geometry" herein is meant that the metal atom is forced to greater exposure of the active metal site because of one or more substituents on the cyclopentadienyl or substituted cyclopentadienyl group forming a portion of a ring structure wherein the metal is both bonded to an adjacent covalent moiety and is held in association with the cyclopentadienyl or substituted cyclopentadienyl group through an η^5 or other π -bonding interaction. It is understood that each respective bond between the metal atom and the constituent atoms of the cyclopentadienyl or substituted cyclopentadienyl group need not be equivalent. That is, the metal may be symmetrically or unsymmetrically π -bound to the cyclopentadienyl or substituted cyclopentadienyl group.

50 The geometry of the active metal site is further defined as follows. The centroid of the cyclopentadienyl or substituted cyclopentadienyl group may be defined as the average of the respective X, Y, and Z coordinates of the atomic centers forming the cyclopentadienyl or substituted cyclopentadienyl group. The angle, θ , formed at the metal center between the centroid of the cyclopentadienyl or substituted cyclopentadienyl group and each other ligand of the metal complex may be easily calculated by standard techniques of single crystal X-ray diffraction. Each of these angles may increase or decrease depending on the molecular structure of the constrained geometry metal complex. Those complexes wherein one or more of the angles, θ , is less than in a similar, comparative complex differing only in the fact that the constrain-inducing substituent is replaced by hydrogen have constrained geometry for purposes of the present invention. Preferably one or more of the above

angles, θ , decrease by at least 5 percent, more preferably 7.5 percent, compared to the comparative complex. Highly preferably, the average value of all bond angles, θ , is also less than in the comparative complex.

Preferably, monocyclopentadienyl metal coordination complexes of group 4 or lanthanide metals according to the present invention have constrained geometry such that the smallest angle, θ , is less than 115° , more preferably less than 110° , most preferably less than 105° .

Highly preferred derivative compounds are monocyclopentadienyl compounds corresponding to the formula:



wherein:

M is titanium or zirconium;

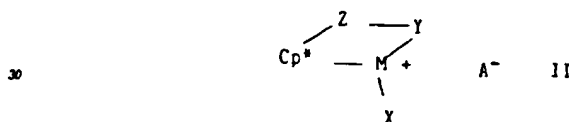
Cp* is a cyclopentadienyl or substituted cyclopentadienyl group bound in an η^5 bonding mode to M;

Z is a divalent moiety comprising oxygen, boron, or a member of group 14 of the Periodic Table of the Elements;

Y is a linking group comprising nitrogen, phosphorus, oxygen or sulfur or optionally Z and Y together form a fused ring system; and

X is as previously defined.

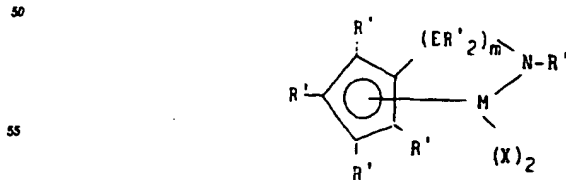
After molecular oxidation, the highly preferred catalysts of the invention correspond to the formula:



wherein Cp*, Z, M, X and A⁻ are as previously defined.

Each carbon atom in the cyclopentadienyl radical may be substituted or unsubstituted with the same or a different radical selected from the group consisting of hydrocarbyl radicals, substituted-hydrocarbyl radicals wherein one or more hydrogen atoms is replaced by a halogen atom, hydrocarbyl-substituted metalloids wherein the metalloid is selected from Group 14 of the Periodic Table of the Elements, and halogen radicals. In addition two or more such substituents may together form a fused ring system. Suitable hydrocarbyl and substituted-hydrocarbyl radicals, which may be substituted for at least one hydrogen atom in the cyclopentadienyl radical, will contain from 1 to 20 carbon atoms and include straight and branched alkyl radicals, cyclic hydrocarbon radicals, alkyl-substituted cyclic hydrocarbon radicals, aromatic radicals and alkyl-substituted aromatic radicals. Suitable organometalloid radicals include mono-, di- and trisubstituted organometalloid radicals of Group 14 elements wherein each of the hydrocarbyl groups contain from 1 to 20 carbon atoms. More particularly, suitable organometalloid radicals include trimethylsilyl, triethylsilyl, ethyldimethylsilyl, methyldiethylsilyl, triphenylgermyl, trimethylgermyl and the like.

Most highly preferred derivative compounds are amidosilane- or amidoalkanedyl- compounds corresponding to the formula:



wherein:

M is titanium or zirconium, bound to an η^5 -cyclopentadienyl group;

R' each occurrence is independently selected from hydrogen, silyl, alkyl, aryl and combinations thereof having up to 10 carbon or silicon atoms;

E is silicon or carbon;

X independently each occurrence is hydride, alkyl, or aryl of up to 10 carbons; and

m is 1 or 2.

Examples of the above most highly preferred metal coordination compounds include compounds wherein the R' on the amido group is methyl, ethyl, propyl, butyl, pentyl, hexyl, (including isomers), norbornyl, benzyl, phenyl, etc.; the cyclopentadienyl group is cyclopentadienyl, indenyl, tetrahydroindenyl, fluorenyl, octahydrofluorenyl, etc.; R' on the foregoing cyclopentadienyl groups each occurrence is hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, (including isomers), norbornyl, benzyl, phenyl, etc.; and X is methyl, neopentyl, trimethylsilyl, norbornyl, benzyl, methylbenzyl, phenyl, etc. Specific compounds include: (tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl)-1,2-ethanediytitanium dimethyl, (tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl)-1, 2-ethanediyttitanium dimethylbenzyl, (methylamido)(tetramethyl- η^5 -cyclopentadienyl)-1,2-ethanediytitanium dibenzhydrazyl, (methylamido)(tetramethyl- η^5 -cyclopentadienyl)-1,2-ethanediyttitanium dineopentyl, (ethylamido)(tetramethyl- η^5 -cyclopentadienyl)-methylphenyltitanium diphenyl, (tert-butylamido)dibenzyl(tetramethyl- η^5 -cyclopentadienyl)silanezirconium dibenzyl, (benzylamido)dimethyl-(tetramethyl- η^5 -cyclopentadienyl)silanezirconium di(trimethylsilyl) and (phenylphosphido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silanezirconium dibenzyl.

In the most preferred embodiment Z-Y is an amidosilane or amidoalkane group of up to 10 nonhydrogen atoms, that is, (tert-butylamido)(dimethylsilyl), (tert-butylamido)-1-ethane-2-yl, etc.

Derivative compounds which may be used in the preparation of the improved catalyst of this invention are covalently bonded metal compounds that are either devoid of reactive hydrogens (other than hydride leaving groups, X) or wherein potentially reactive hydrogens are protected by bulky protecting groups. Examples of suitable organyl substituents on such metal derivative compounds include norbornyl, neopentyl, trimethylsilyl and diphenylmethyl. Illustrative, but not limiting examples of suitable derivative compounds include: tetranorbornyltitanium, tetrabenzylzirconium, tetra-neopentyltitanium, diphenoxymethylzirconium, bis(2,6-diisopropyl-4-methylphenoxy)dibenzyltitanium, tris(tert-butylsiloxy)trimethylzirconium, dimethoxydibenzhydrazyltitanium, bis(2,4,6-trimethylphenoxy)dibenzyltitanium, butoxybis(trimethylsilyl)methylzirconium, dinorbornyl-dimethyltitanium, tribenzyltitanium hydride, etc.; cyclopentadienyl and bis(cyclopentadienyl) metal compounds such as bis(cyclopentadienyl)dimethylzirconium, cyclopentadienyltribenzylzirconium, cyclopentadienyl-trimethyltitanium, cyclopentadienyltrimethylzirconium, bis(cyclopentadienyl) dineopentyltitanium, cyclopentadienyltri(diphenylmethyl)zirconium, bis(cyclopentadienyl)diphenylzirconium, cyclopentadienyltrineopentyl-titanium, bis(cyclopentadienyl)di(m-tolyl)zirconium, bis(cyclopentadienyl)di(p-tolyl)zirconium; hydrocarbyl-substituted cyclopentadienyl or bis(cyclopentadienyl) compounds such as (pentamethylcyclopentadienyl)(cyclopentadienyl) dimethylzirconium, bis(ethylcyclopentadienyl)dimethylzirconium, (pentamethylcyclopentadienyl)tribenzylzirconium, (n-butylcyclopentadienyl)trineopentyltitanium, cyclopentadienyltrimethyltitanium hydride, bis(cyclopentadienyl)bis(diphenylmethyl)zirconium, bis(tert-butylcyclopentadienyl)bis(trimethylsilylmethyl)zirconium, bis(cyclohexylcyclopentadienyl) dimethylzirconium, (benzylcyclopentadienyl)di(m-tolyl)methyltitanium, (diphenylcyclopentadienyl)dinorbornylmethylzirconium, bis(methylcyclopentadienyl)diphenylzirconium, (tetraethylcyclopentadienyl)tribenzylzirconium, (propylcyclopentadienyl) (cyclopentadienyl) dimethylzirconium, bis(propylcyclopentadienyl)dimethylzirconium, (n-butylcyclopentadienyl) dimethyl(n-butoxy)titanium, cyclopentadienyl(diphenylisopropoxy)zirconium, cyclohexylmethylcyclopentadienyl cyclopentadienyltribenzylzirconium, bis((cyclohexyl)methylcyclopentadienyl)dibenzylzirconium, bis(cyclopentadienyl) zirconium dihydride, benzylcyclopentadienyltrimethylhafnium, bis(indenyl)dibenzylzirconium, (tert-butylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silane dibenzylzirconium, (benzylamido)dimethyl(tetraethyl- η^5 -cyclopentadienyl)silane dibutyltitanium, and the like; metal hydrocarbyl-substituted cyclopentadienyl metal compounds such as ((trimethylsilyl)cyclopentadienyl)trimethylzirconium, bis((trimethylgermyl)cyclopentadienyl)dimethyltitanium, ((trimethylstannyl)cyclopentadienyl)tribenzylzirconium, ((pentamethylsilyl)cyclopentadienyl)(cyclopentadienyl)dimethylzirconium, bis((trimethylsilyl)cyclopentadienyl)dimethylzirconium, pentamethylsilyl(cyclopentadienyl)tribenzyltitanium, bis((trimethylgermyl)cyclopentadienyl)diphenylhafnium; halogen-substituted cyclopentadienyl compounds such as ((trifluoromethyl)cyclopentadienyl)(cyclopentadienyl)dimethylzirconium, bis((trifluoromethyl)cyclopentadienyl)dinorbornylzirconium, ((trifluoromethyl)cyclopentadienyl)tribenzylzirconium; silyl-substituted (cyclopentadienyl)metal compounds such as bis(cyclopentadienyl)di(trimethylsilyl)zirconium, cyclopentadienyltri(phenyldimethylsilyl)zirconium; bridged cyclopentadienyl-metal compounds such as methylenebis((cyclopentadienyl)dimethylzirconium), ethylene-bis-((cyclopentadienyl)dibenzylzirconium), (dimethylsilylene)-bis-((cyclopentadienyl)dimethyltitanium), methylene-bis-((cyclopentadienyl) di(trimethylsilyl)zirconium), (dimethylsilylene) bis(cyclopentadienyldineopentylhafnium),

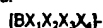
ethylene-bis-(tetrahydroindenyl)-zirconium dibenzyl and dimethylsilylene(fluorenyl)(cyclopentadienyl)-lithium dimethyl.

Other compounds which are useful in the catalyst compositions of this invention, especially compounds containing other Group 4 or Lanthanide metals, will, of course, be apparent to those skilled in the art.

5 Compounds useful as oxidizing agents in the preparation of the compounds of this invention will comprise a cationic oxidizer, and one or more compatible noncoordinating anions, as previously explained.

In a preferred embodiment A⁻ of previous formula (I) comprises an anion which is a single coordination complex comprising a plurality of lipophilic radicals covalently coordinated to and shielding a central formally charge-bearing metal or metalloid atom, which anion is bulky and stable under the oxidation and subsequent
10 polymerization conditions, and which anion is compatible with and noncoordinating towards the resulting Group 4 or Lanthanide metal containing catalyst. The anion is employed only to provide charge balance without interfering with the oxidizing ability of Ox⁺ or the catalytic properties of the resulting catalyst. Any metal or metalloid capable of forming a coordination complex which is stable under the reaction conditions of the present invention may be contained in the anion. Suitable metals include, but are not limited to, aluminum, gold and platinum.
15 Suitable metalloids include, but are not limited to, boron, phosphorus and silicon. Oxidizing agents containing anions comprising a coordination complex containing a single boron atom are most preferred.

Anions comprising boron which are particularly useful in the preparation of catalysts of this invention may be represented by the following general formula:



20 wherein:

B is boron in a valence state of 3;

X₁ to X₄ are the same or different nonreactive, organyl or silyl radicals containing from 6 to 20 carbon or silicon atoms. In addition two or more of X₁ to X₄ may be linked to each other through a stable bridging group. Preferably X₁ to X₄ lack reactive hydrogen moieties. That is, the radicals are either devoid of hydrogen, contain
25 only hydrogen in nonactivated positions or contain sufficient steric hindrance to protect potentially active hydrogen sites. Examples of suitable radicals for X₁ to X₄ are perfluorinated hydrocarbyl radicals containing from 6 to 20 carbon atoms, 3,4,5-trifluorophenyl, etc.

A most highly preferred compatible, non-coordinating, anion is tetra(pentafluorophenyl)borate.

Suitable organic cationic oxidizers for use according to the present invention include ferrocenium ions, bis-indenyl Fe(III) ions, and cationic derivatives of substituted ferrocene, and the like molecules. Suitable metal
30 cationic oxidizers include Ag⁺, Pd²⁺, Pt²⁺, Hg²⁺, Hg₂²⁺, Au⁺ and Cu⁺. Most preferred cationic oxidizers are ferrocenium and Ag⁺ cations.

Illustrative, but not limiting, examples of oxidizing agents in the preparation of the improved catalysts of this invention are ferrocenium tetra(pentafluorophenyl)borate, gold (I) tetrakis 3,4,5-trifluorophenyl borate, silver
35 tetra(pentafluorophenyl)borate and 1,1'-dimethylferrocenium tetrakis 3,5-bis(trifluoromethyl)phenyl borate.

Similar lists of suitable compounds containing other metals and metalloids which are useful as oxidizing agents (second components) could be made, but such lists are not deemed necessary to a complete disclosure. In this regard, it should be noted that the foregoing list is not intended to be exhaustive and other boron compounds that would be useful as well as useful compounds containing other metals or metalloids would be readily
40 apparent, from the foregoing general equations, to those skilled in the art.

Without wishing to be bound by any particular theory of operation it is believed that the cationic oxidizer causes the molecular oxidation of the Group 4 or Lanthanide metal derivative, and in the process becomes a neutral species. The oxidized metal derivative loses a hydrogen or hydrocarbyl radical (R) by a unimolecular elimination reaction. Two or more such radicals form a hydrogen molecule or a neutral organic species of the
45 formula R_x where x is an integer greater than or equal to 2. These byproducts are of course neutral or noninterfering with any subsequent polymerization reaction and may also be removed from the reaction mixture. This result is much preferred to previously known processes for catalyst activation which resulted in the formation of an amine or similar reaction byproduct.

It should be noted that the two compounds combined for preparation of the active catalyst must be selected
50 so as to avoid transfer of a fragment of the anion, particularly an aryl group, to the metal cation, thereby forming a catalytically inactive species. This could be done by steric hindrance, resulting from substitutions on the groups attached to the Group 4 or Lanthanide metal as well as substitutions on the aromatic carbon atoms of the anion. It follows, then, that Group 4 and Lanthanide metal compounds (first components) comprising, for example, perhydrocarbyl-substituted cyclopentadienyl radicals could be effectively used with a broader range
55 of second compounds than could first components comprising less bulky radicals. As the amount and size of the metal substituents are reduced, however, more effective catalysts are obtained with second compounds containing anions which are more resistant to degradation, such as those with substituents on the meta and/or para positions of the phenyl rings. Another means of rendering the anion more resistant to degradation is affor-

ded by fluorine substitution, especially perfluorosubstitution, in the anion. Second components containing fluoro-substituted stabilizing anions may, then, be used with a broader range of first components.

In general, the catalyst can be prepared by combining the two components in a suitable solvent at a temperature within the range from -100°C to 300°C.

5 The catalyst may be used to polymerize α -olefins and/or acetylenically unsaturated monomers having from 2 to 18 carbon atoms and/or diolefins having from 4 to 18 carbon atoms either alone or in combination. The catalyst may also be used to polymerize α -olefins, diolefins and/or acetylenically unsaturated monomers in combination with other unsaturated monomers. In general, the polymerization may be accomplished at conditions well known in the prior art for Ziegler-Natta or Kaminsky-Sinn type polymerization reactions, that is, temperatures from 0 to 250°C and pressures from atmospheric to 1000 atmospheres (100 MPa). Suspension, solution, slurry or other process condition may be employed if desired. A support may be employed but preferably the catalysts are used in a homogeneous manner. It will, of course, be appreciated that the catalyst system will form *in situ* if the components thereof are added directly to the polymerization process and a suitable solvent or diluent, including condensed monomer, is used in said polymerization process. It is, however, preferred to form the catalyst in a separate step in a suitable solvent prior to adding the same to the polymerization mixture.

As indicated supra, the improved catalyst of the present invention will, preferably, be prepared in a suitable solvent or diluent. Suitable solvents or diluents include any of the solvents known in the prior art to be useful as solvents in the polymerization of olefins, diolefins and acetylenically unsaturated monomers. Suitable solvents include straight and branched-chain hydrocarbons such as isobutane, butane, pentane, hexane, heptane, octane, and mixtures thereof; cyclic and alicyclic hydrocarbons such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, perfluorinated hydrocarbons such as perfluorinated C_{4-10} alkanes and aromatic and alkyl-substituted aromatic compounds such as benzene, toluene and xylene. Suitable solvents also include liquid olefins which may act as monomers or comonomers including ethylene, propylene, butadiene, cyclopentene, 1-hexene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1,4-hexadiene, 1-octene, 1-decane, styrene, divinylbenzene, allylbenzene and vinyltoluene (including all isomers alone or in admixture).

25 It is believed that the active catalyst species of the present invention contains a metal center which center remains cationic, unsaturated and has a metal-carbon bond which is reactive with olefins, diolefins and acetylenically unsaturated compounds. Also associated with this metal center is a charge balancing anionic remnant of the formula A^- .

30 The catalyst formed by the method of this invention may be retained in solution or separated from the solvent, isolated, and stored for subsequent use. As previously indicated supra, the catalyst may also be prepared *in situ* during a polymerization reaction by passing the separate components into the polymerization vessel where the components will contact and react to produce the improved catalyst of this invention.

The equivalent ratio of derivative of a Group 4, or Lanthanide metal compound to oxidizing agent compound employed is preferably in a range from 0.1:1 to 10:1, more preferably from 0.75:1 to 2:1, most preferably 1.0:1.0. In most polymerization reactions the equivalent ratio of catalyst:polymerizable compound employed is from 10⁻¹²:1 to 10⁻¹:1, more preferably from 10⁻⁶:1 to 10⁻³:1.

A beneficial feature of some of the catalysts of this invention, particularly those based on monocyclopentadienyl substituted titanium compounds in combination with an oxidizing agent comprising boron, is that when the catalysts of this invention are used to copolymerize α -olefins, either alone or in combination with diolefins, the amount of higher molecular weight olefin or diolefin incorporated into the copolymer is significantly increased when compared to copolymers prepared with the more conventional Ziegler-Natta type catalysts. The relative rates of reaction of ethylene and higher α -olefins with the aforementioned titanium-based catalysts of this invention are so similar that the monomer distribution in copolymers prepared with the catalysts of this invention may be controlled by the ratio of monomeric reactants.

45 "Addition polymerizable monomers" usefully polymerized according to the present invention include, for example, ethylenically unsaturated monomers, acetylenic compounds, conjugated or nonconjugated dienes, polyenes, carbon monoxide, etc. Preferred monomers include the C_{2-10} α -olefins especially ethylene, propylene, isobutylene, 1-butene, 1-hexene, 4-methyl-1-pentene, and 1-octene. Other preferred monomers include styrene, halo- or alkyl substituted styrenes, tetrafluoroethylene, vinylbenzocyclobutane, and 1,4-hexadiene.

In general, catalysts can be selected so as to produce polymer products which will be free of certain trace impurities such as aluminum, magnesium and chloride generally found in polymers produced with Ziegler-Natta type catalysts. The polymer products produced with the catalysts of this invention should, then, have a broader range of applications than polymers produced with more conventional Ziegler-Natta type catalysts comprising a metal alkyl such as an aluminum alkyl.

Having described the invention the following examples are provided as further illustration thereof and are

not to be construed as limiting. Unless stated to the contrary all parts and percentages are expressed on a weight basis.

Example 1

A catalyst mixture was prepared by combining 50 micromoles of bis(cyclopentadienyl)dibenzylzirconium and 50 micromoles of ferrocenium perfluorotetraphenyl borate in 50 ml purified and deaerated toluene. The mixture was agitated for approximately 30 seconds until the blue ferrocenium coloration was discharged.

Polymerization

The catalyst was combined with a mixture comprising 2 L of mixed alkane solvent (Isopar E™ available from Exxon Chemicals Inc.), 75 ml at 50 psi (350 kPa) of hydrogen, and ethylene (31 atmospheres, 3.1 MPa) in a 4 L reactor. The reactants were previously deaerated and purified and the reactor contents were heated to 170°C. Ten milliliters of the catalyst solution of Example 1 were added. An immediate rapid uptake of ethylene and considerable rise in reactor temperature occurred. (The ethylene uptake was greater than 100 g per minute and the temperature rise was greater than 17°C). At the end of a 10 minute reaction period the reactor contents were removed and devolatilized leaving 46 g of high density polyethylene.

Example 2

To 25 ml of deaerated purified toluene, 25 micromoles of (tert-butylamido)dimethyl(tetramethyl- η^5 cyclopentadienyl)silane dibenzylzirconium and 25 micromoles of ferrocenium perfluorotetraphenyl borate were added. The mixture was agitated for approximately 1 minute until the blue color of the solid ferrocenium salt was discharged.

Polymerization

A 4 L reactor was charged with 2 L of mixed alkane solvent (Isopar E™) and 300 ml of 1-octene, heated to 150°C and pressurized with ethylene to 31 atmospheres (3.1 MPa). All components had been previously deaerated and purified. 20 ml of the above catalyst solution were added resulting in an immediate rapid uptake of ethylene and a large rise in reactor temperature (approximately 50 g per minute ethylene uptake and temperature rise of 26°C). At the end of a 10 minute period the reactor contents were removed and devolatilized leaving 78 g of ethylene/1-octene copolymer. The 1-octene content of the polymer was 7.5 mole percent as determined by mass balance.

Example 3

A catalyst solution was prepared by mixing 10 micromoles each of (tertbutylamido)dimethyl (η^5 -2,3,4,5-tetramethylcyclopentadienyl)silane dibenzyl titanium and ferrocenium perfluorotetraphenylborate in 5 milliliters of toluene. After thirty seconds of agitation the blue ferrocenium had been consumed and a greenish brown solution formed.

Polymerization

Addition of this catalyst solution to a stirred (500 rpm) two liter reactor containing Isopar-E (1000 ml), 1-octene (200 ml), hydrogen (50 ml @ 50 psi, 350 kPa) and ethylene (saturated @ 450 psi, 3 MPa) at 130°C resulted in a 40°C temperature rise. Ten minutes after addition of the catalyst solution to the reactor the contents were removed from the reactor and the volatiles stripped to give 104 g of linear low density polyethylene.

Example 4

A catalyst mixture was prepared from 10 micromoles each of ferrocenium perfluorotetraphenylborate and 2-(η^5 -cyclopentadienyl)-2-(η^5 -fluorenyl) propane dibenzyl zirconium in toluene (5 ml). A greenish solution was obtained after 1 minute of agitation.

Polymerization

This catalyst solution was then added to a stirred (500 rpm) 2 liter reactor containing propylene (200 g), Isopar-E (600 ml), and 1-octene (200 ml) at 50°C. A temperature rise of 10°C occurred upon addition of catalyst and was maintained for 3 minutes despite circulation of a -10°C ethylene glycol/water mixture through the reactor's internal cooling coils. After 30 minutes the contents of the reactor were removed and devolatilized to give 167 g of clear, rubbery, syndiotactic propylene/1-octene copolymer.

10 Claims

1. A process for preparing an addition polymerization catalyst of the formula:



wherein:-

- 15 L independently each occurrence is a ligand or ligand system;
 M is a metal of Group 4 or the Lanthanide series of the Periodic Table of the Elements;
 X is hydride or a hydrocarbyl, silyl or germyl group having up to 20 carbon, silicon or germanium atoms;
 f is an integer greater than or equal to 1, and
 20 A⁻ is a monovalent compatible noncoordinating anion,
 comprising contacting a derivative of a Group 4 or Lanthanide metal corresponding to the formula:



wherein:-

- 25 L, f, M and each X independently are as defined above with an oxidizing agent which in reduced form is noninterfering with the resulting catalyst, said oxidising agent corresponding to the formula:
 $(Ox^{+a})_b (A^-)_d$

wherein:-

- Ox^{+a} is a non-Bronsted acid, cationic oxidizer having a charge of (+a) capable of oxidizing the derivative of a Group 4 or Lanthanide metal;
 30 A⁻ is as previously defined; and
 b and d are integers selected to provide charge balance.

2. A process as claimed in Claim 1, wherein the cationic oxidizer has an oxidation potential of at least +0.20 volt.
- 35 3. A process as claimed in Claim 2, wherein the cationic oxidizer has an oxidation potential is at least +0.25 volt.
4. A process as claimed in any one of the preceding claims, wherein Ox^{+a} is selected from ferrocenium; bis-Indenyl Fe(III); cationic derivatives of substituted ferrocenium; and metallic cations.
- 40 5. A process as claimed in Claim 4, wherein Ox^{+a} is ferrocenium or Ag⁺.
6. A process as claimed in any one of the preceding claims, wherein A⁻ is:
- 45 $[BX_1X_2X_3X_4]^-$
- wherein:
 B is boron in a valence state of 3.
 X₁ to X₄ are the same or different nonreactive, organyl or silyl radicals containing from 6 to 20 carbon or silicon atoms and optionally two or more of X₁ to X₄ may be linked to each other through a stable bridging group.
- 50 7. A process as claimed in Claim 6, wherein X₁, X₂, X₃, X₄ are perfluorinated hydrocarbyl radicals containing from 6 to 20 carbons.
8. A process as claimed in any one of the preceding claims, wherein M is titanium or zirconium.
9. A process as claimed in any one of the preceding claims, wherein L is:
 a) an anionic ligand selected from the group consisting of, R, -R'(OR)_mOR, (OR)_mOR, -PR₂, -SR, -OR,

-NR₂, hydride, and organometaloid radicals comprising a Group 14 element wherein each of the hydrocarbyl substituents contained in the organic portion of said organometaloid, independently, contains from 1 to 20 carbon atoms, wherein

R is a hydrocarbyl, silyl, germyl or a substituted hydrocarbyl, silyl, or germyl group of from 1 to 24 carbon, silicon, or germanium atoms;

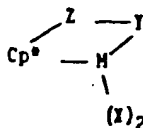
R' is C₂₋₁₀ alkylene, and

m is an integer from zero to ten; or

b) a neutral donor ligand selected from the group consisting of, ROR, NR₃, PR₃, and SR₂ wherein R is as above defined.

10. A process as claimed in any one of the preceding claims, wherein L is a derivative of a substituted cyclopentadienyl group imparting a constrained geometry to the metal active site and containing up to 20 nonhydrogen atoms.

11. A process as claimed in Claim 10, wherein L₁ MX₂ corresponds to the formula:



wherein:

M is titanium or zirconium;

X is as defined in Claim 1;

Cp* is a cyclopentadienyl or substituted cyclopentadienyl group bound in an η⁵ bonding mode to M;

Z is a divalent moiety comprising oxygen, boron, or a member of Group 14 of the Periodic Table of the Elements; and

Y is a linking group comprising nitrogen, phosphorus, oxygen or sulfur or optionally Z and Y together form a fused ring system.

12. A process as claimed in Claim 11, wherein each X independently is hydride, alkyl or aryl of up to 10 carbon atoms; Y is NR'; and Z is (ER'₂)_m, wherein each R' independently is hydrogen, silyl, alkyl, aryl or a combination thereof having up to 10 carbon or silicon atoms; and m is 1 or 2.

13. A process as claimed in any one of the preceding claims, wherein X is hydride or C₁-C₁₀ hydrocarbyl.

14. A process as claimed in Claim 13, wherein X is benzyl.

15. An addition polymerization catalyst substantially lacking in amine or phosphine byproducts and corresponding to the formula:



wherein:

L independently each occurrence is a ligand or ligand system;

M is a metal of Group 4 or Lanthanide series of the Periodic Table of the Elements;

X is hydride or a hydrocarbyl, silyl or germyl group having up to 20 carbon, silicon or germanium atoms;

f is an integer greater than or equal to 1; and

A⁻ is a monovalent compatible noncoordinating anion.

16. A catalyst as claimed in Claim 15, wherein L, f, M, X, and A⁻ are as defined in any one of Claims 1 to 14.

17. The use as an addition polymerization catalyst of a catalyst as claimed in Claim 15 or Claim 16 or obtained by a process as claimed in any one of Claims 1 to 14.

18. A catalytic addition polymerization process characterized in that the catalyst is as claimed in Claim 15 or

Claim 16 or obtained by a process as claimed in any one of Claims 1 to 14.

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European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 91 30 5955

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	J. AM. CHEM. SOC. vol. 109, 1987, pages 4111 - 4113; R. F. JORDAN: 'CHEMISTRY OF CATIONIC ZIRCONIUM(IV) BENZYL COMPLEXES. ONE ELECTRON OXIDATION OF α ORGANOMETALLICS.'	1	C08F4/74 C08F10/00 C07F7/28 C07F17/00
P, X	EP-A-0 421 659 (THE DOW CHEM. COMP) " page 2, line 47 - page 5, line 20; claim 1 "	1-18	
P, X	EP-A-0 426 637 (FINA) " claims 1, 27 "	1	
A	EP-A-0 277 004 (EXXON) " claims "	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C07F C08F
The present search report has been drawn up for all claims			
Name of search		Date of completion of the search	Examiner
THE HAGUE		13 NOVEMBER 1991	DE ROECK ROO
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, not published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document	